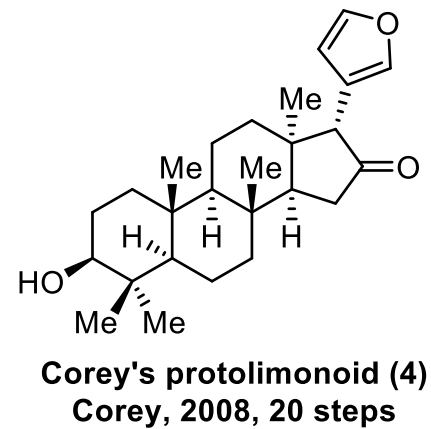
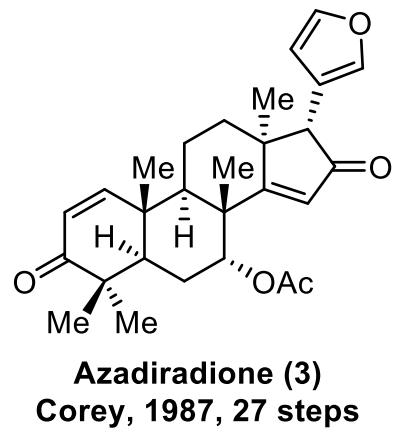
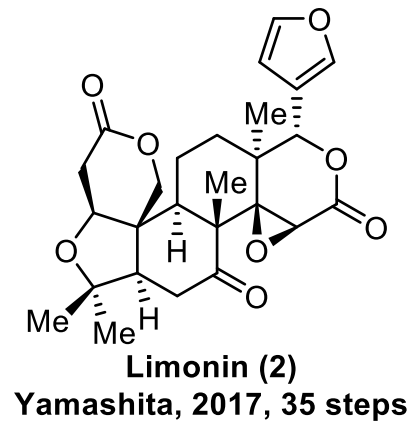
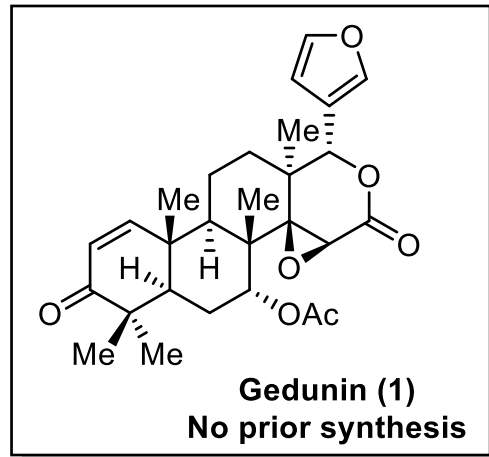


Concise Chemoenzymatic Synthesis of Gedunin

Max Eaton

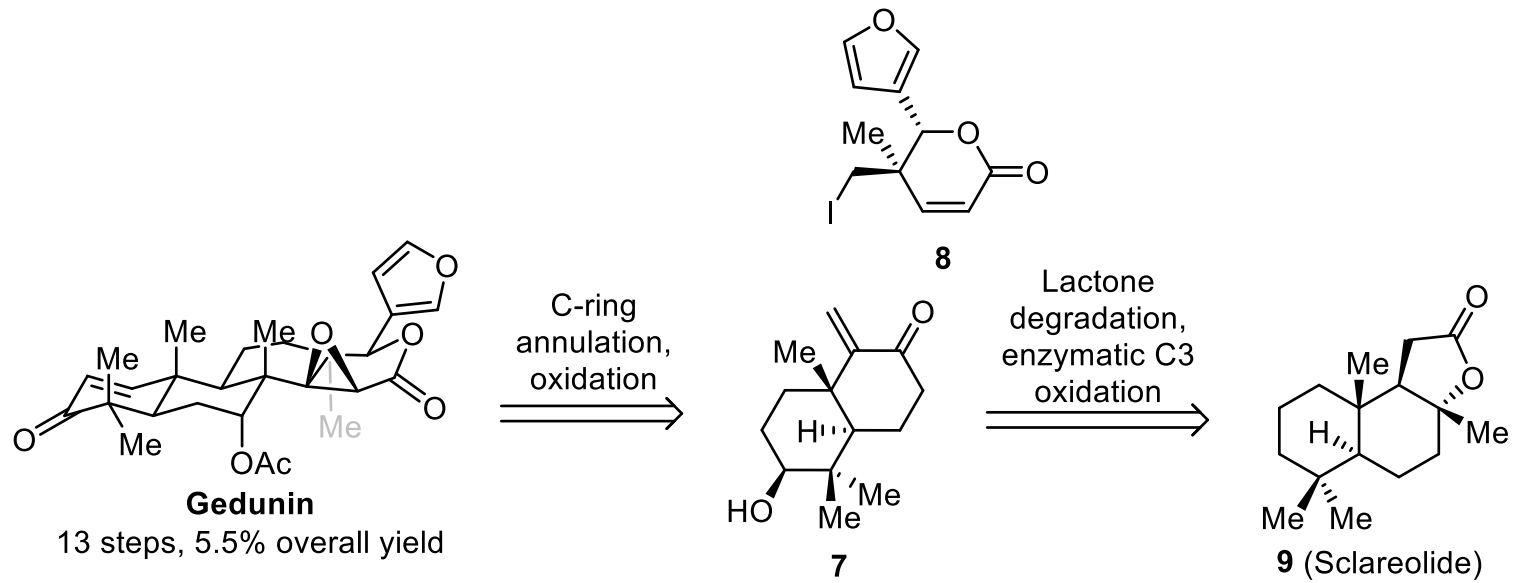
11/2/2022

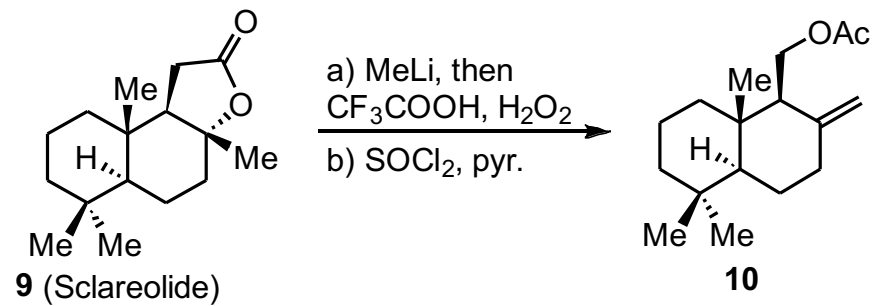
Gedunin (1) and Other Limonoids



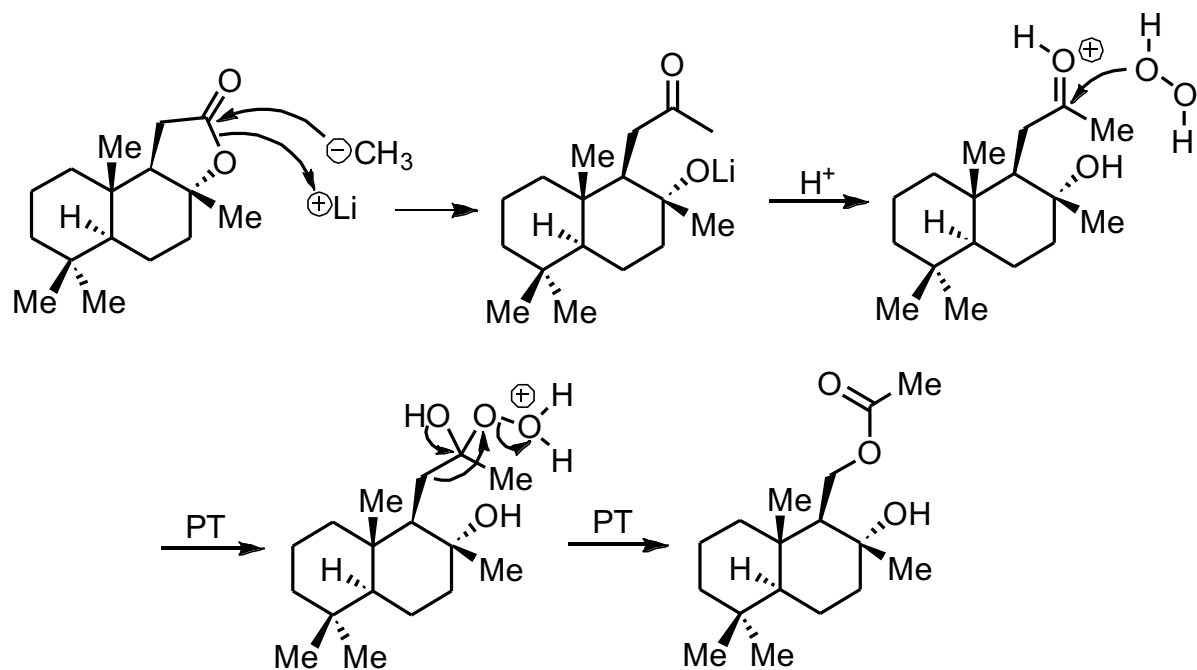
- Several total syntheses of limonoid triterpenes (1-4) have been reported
- Little is known about the biosynthesis of the more complex limonoids
- Many limonoids are known to have notable biological activities

Retrosynthetic Analysis

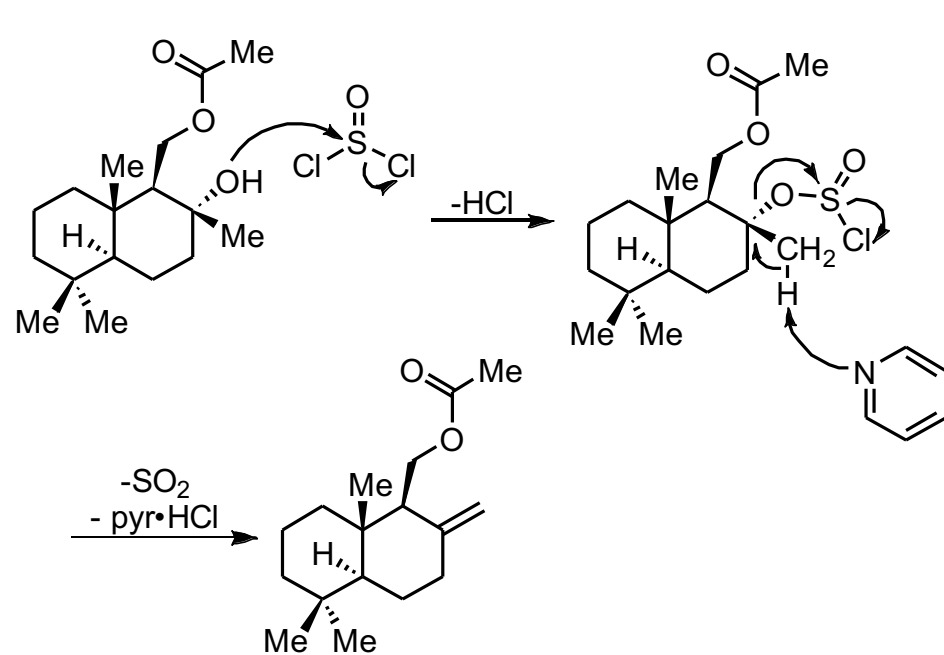


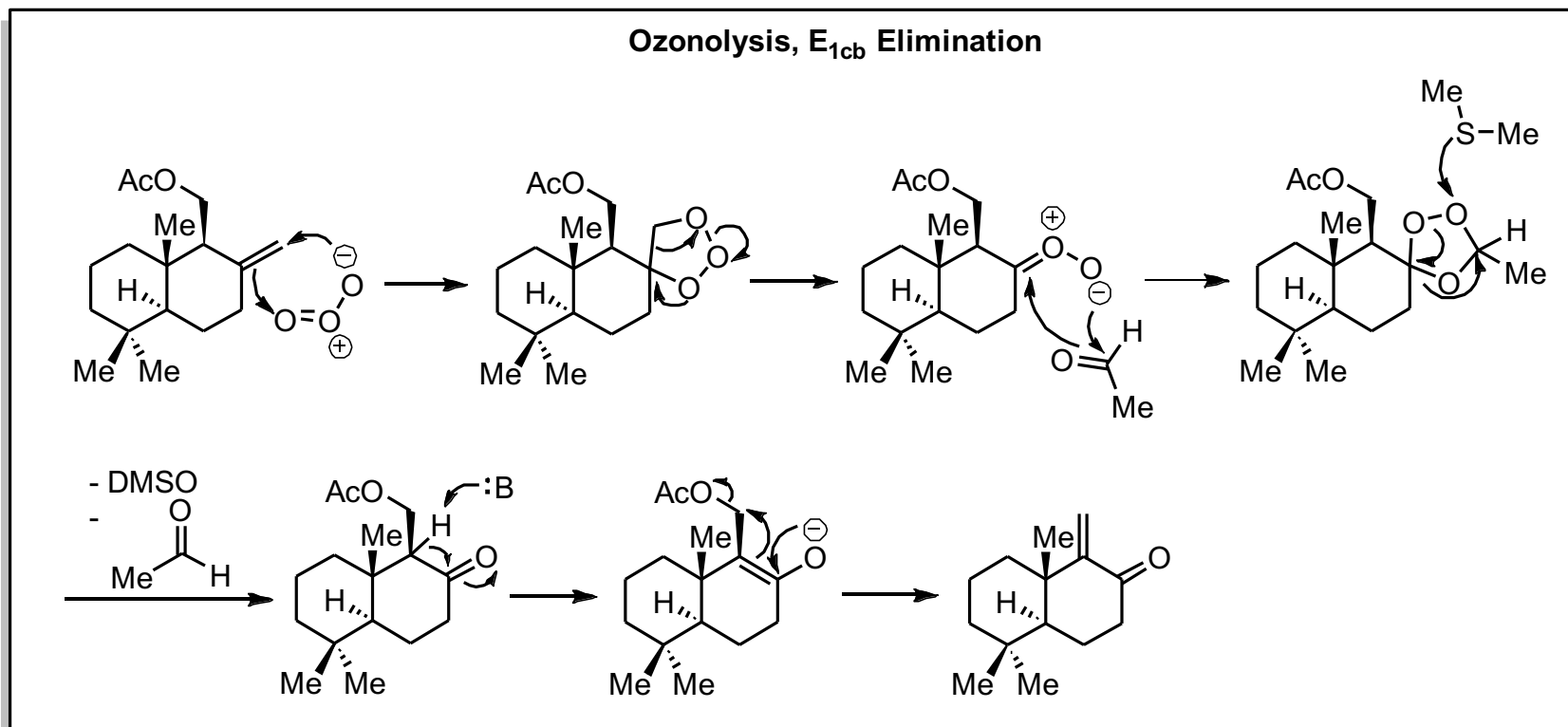
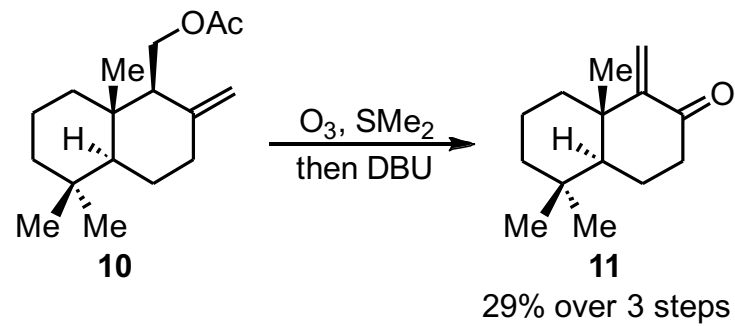


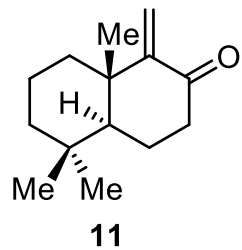
Addition of methyllithium to lactone, Baeyer-Villiger oxidation



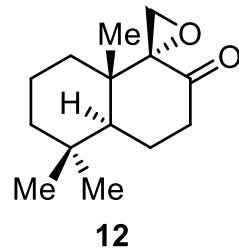
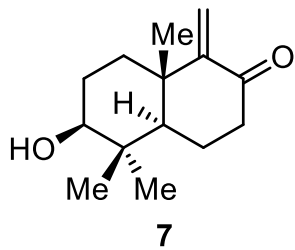
E₂ Elimination





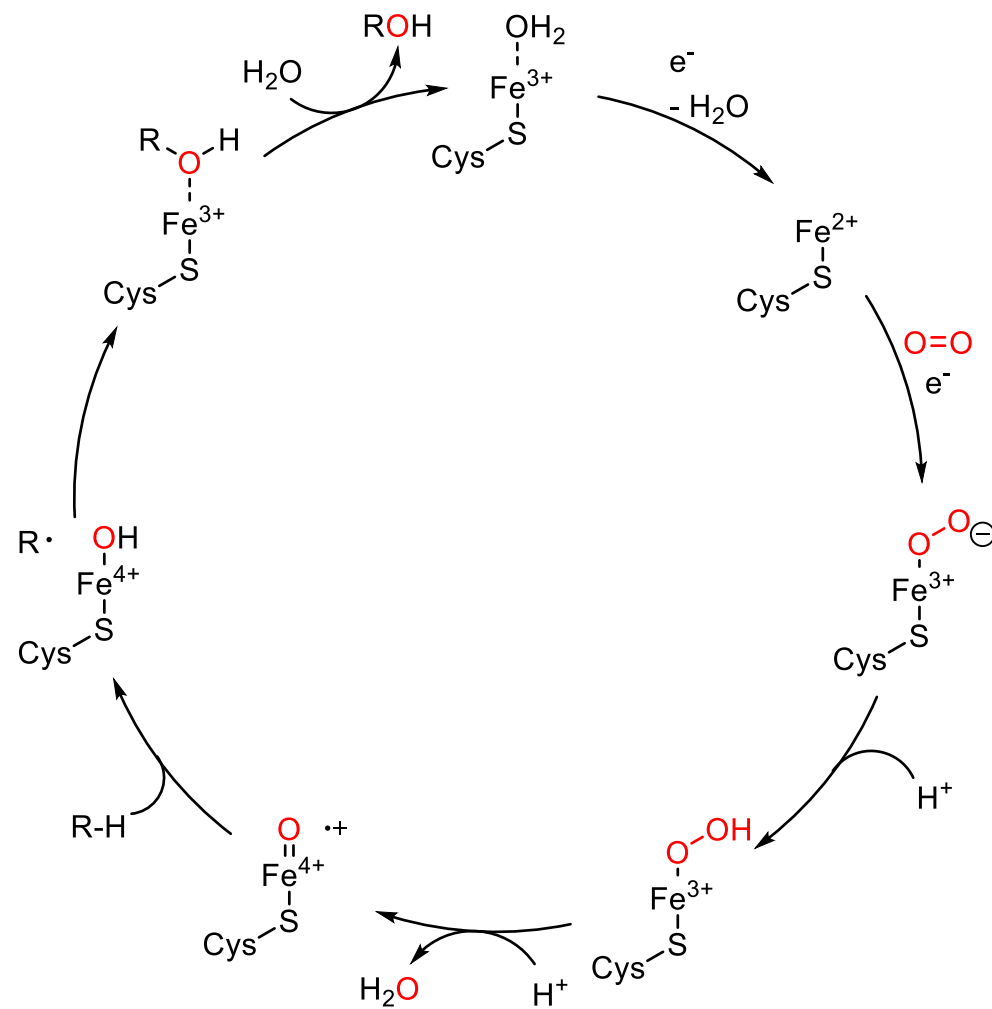


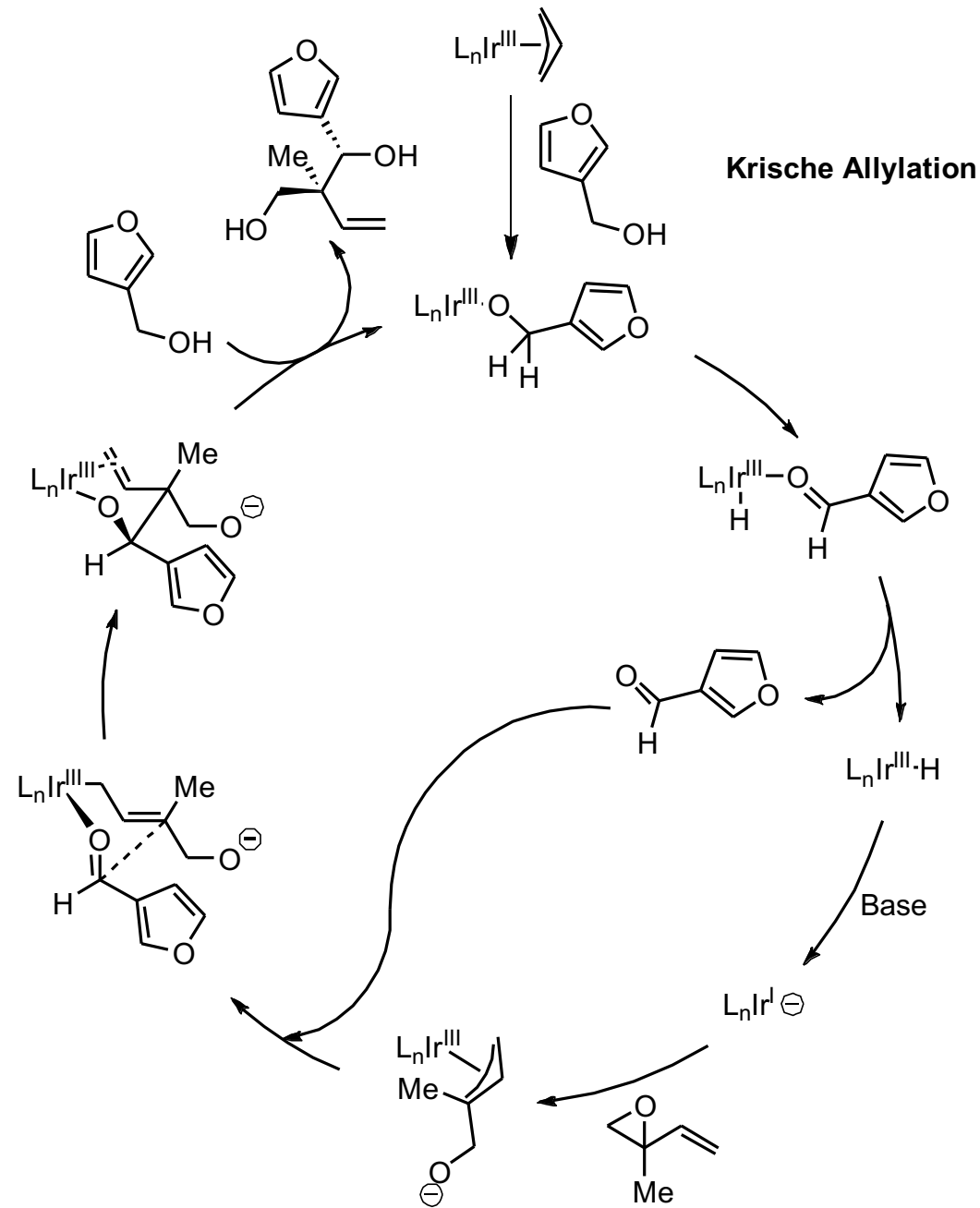
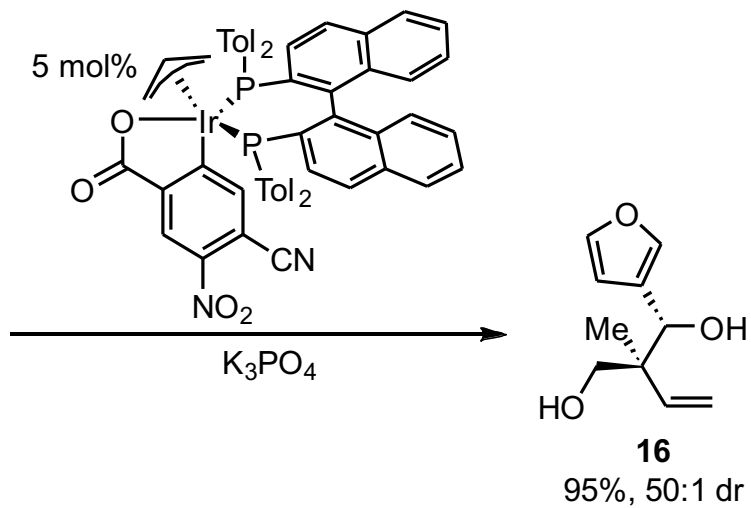
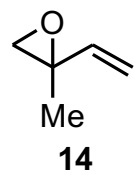
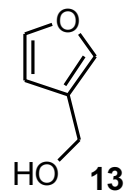
MERO1 L437A

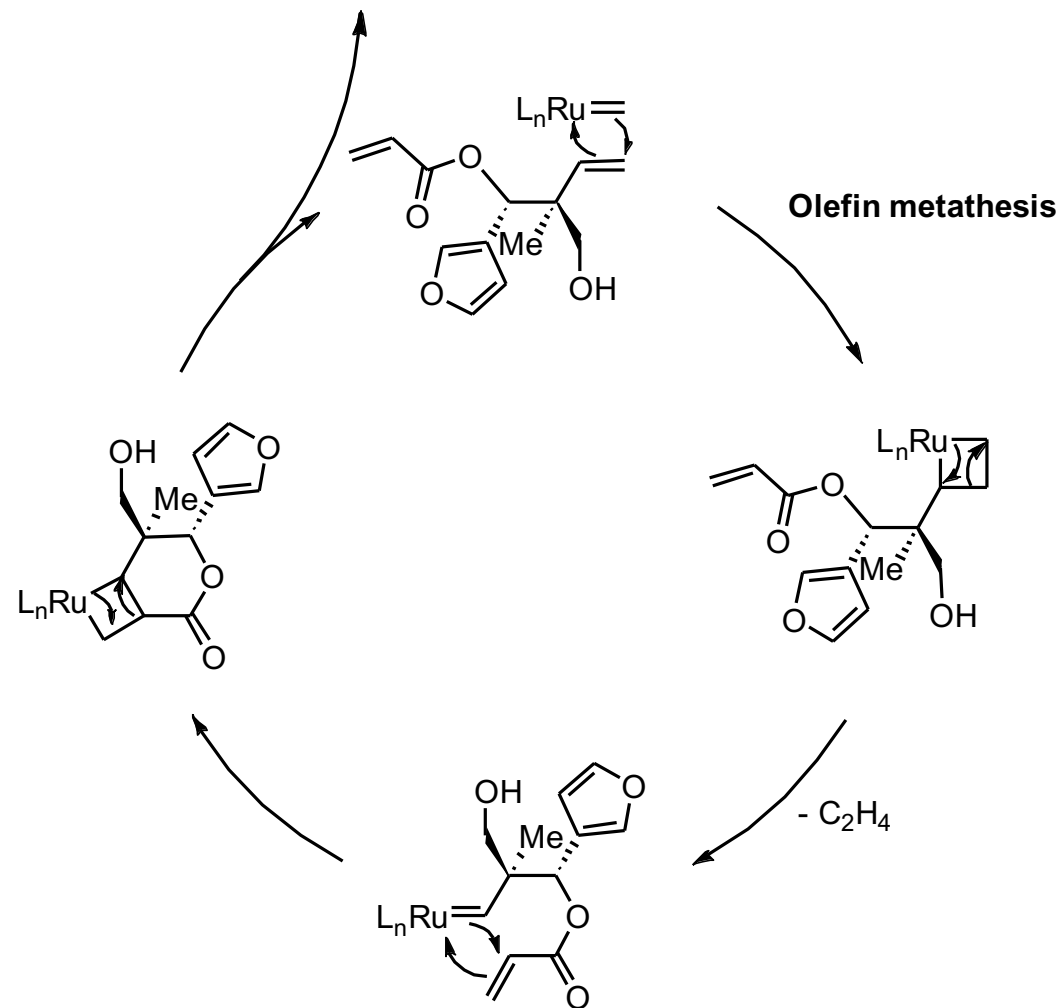
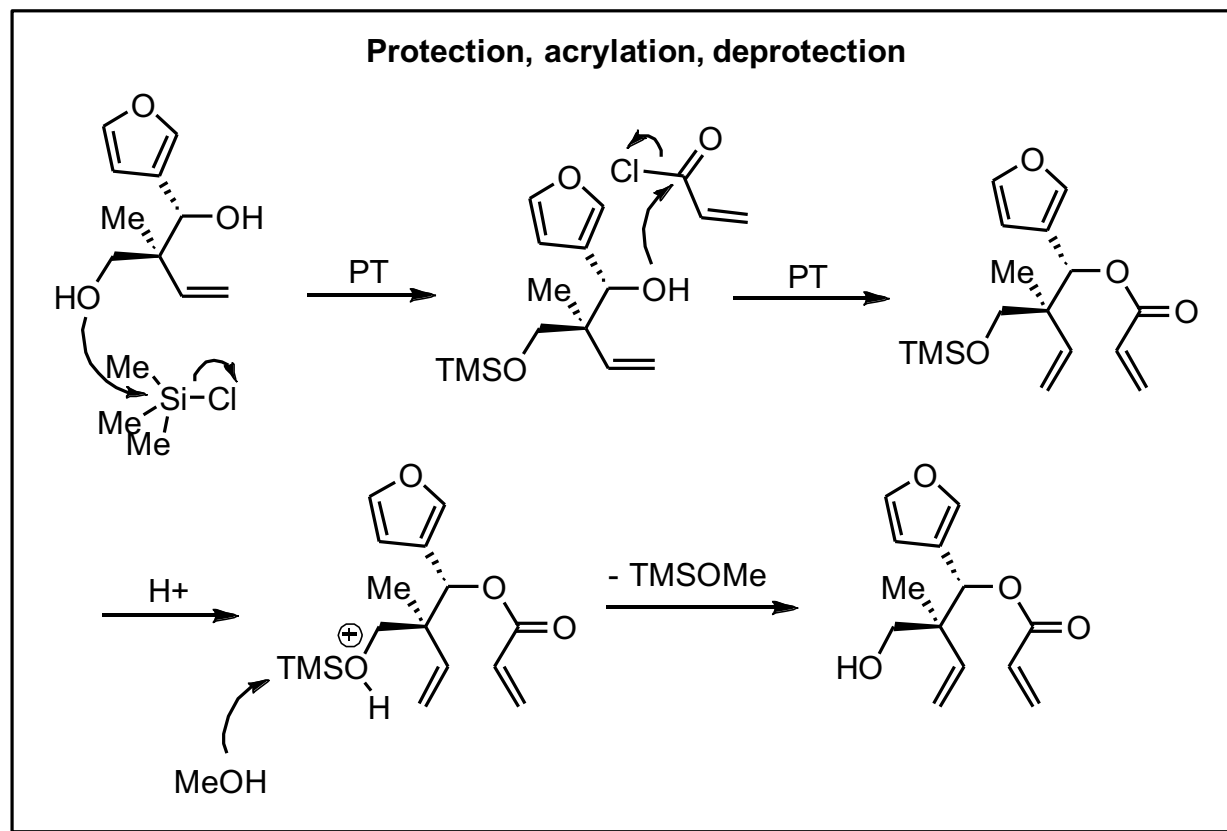
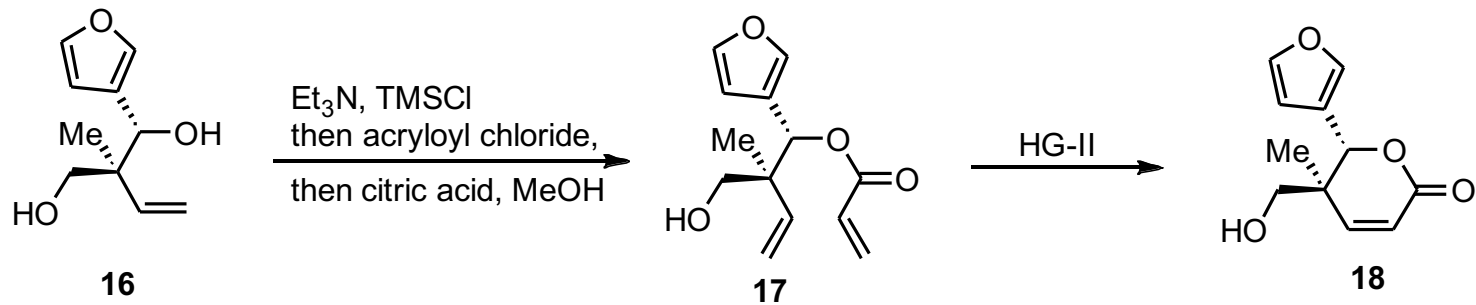


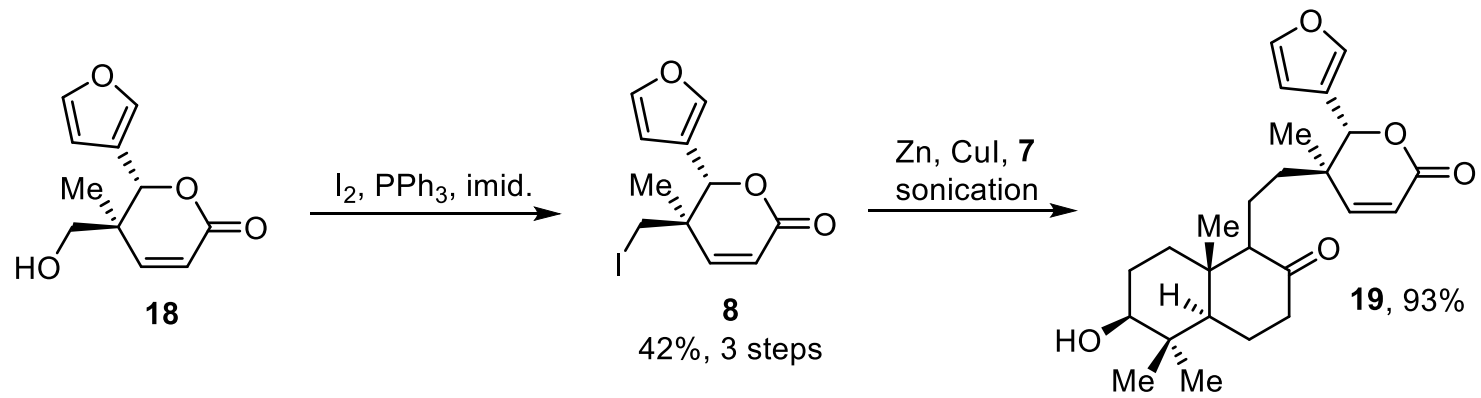
variant	7 (%)	12 (%)
MERO1	27	45
MERO1 L75A	15	5
MERO1 M177A	5	82
MERO1 L437A	68	8

Cytochrome P450-type Oxidation

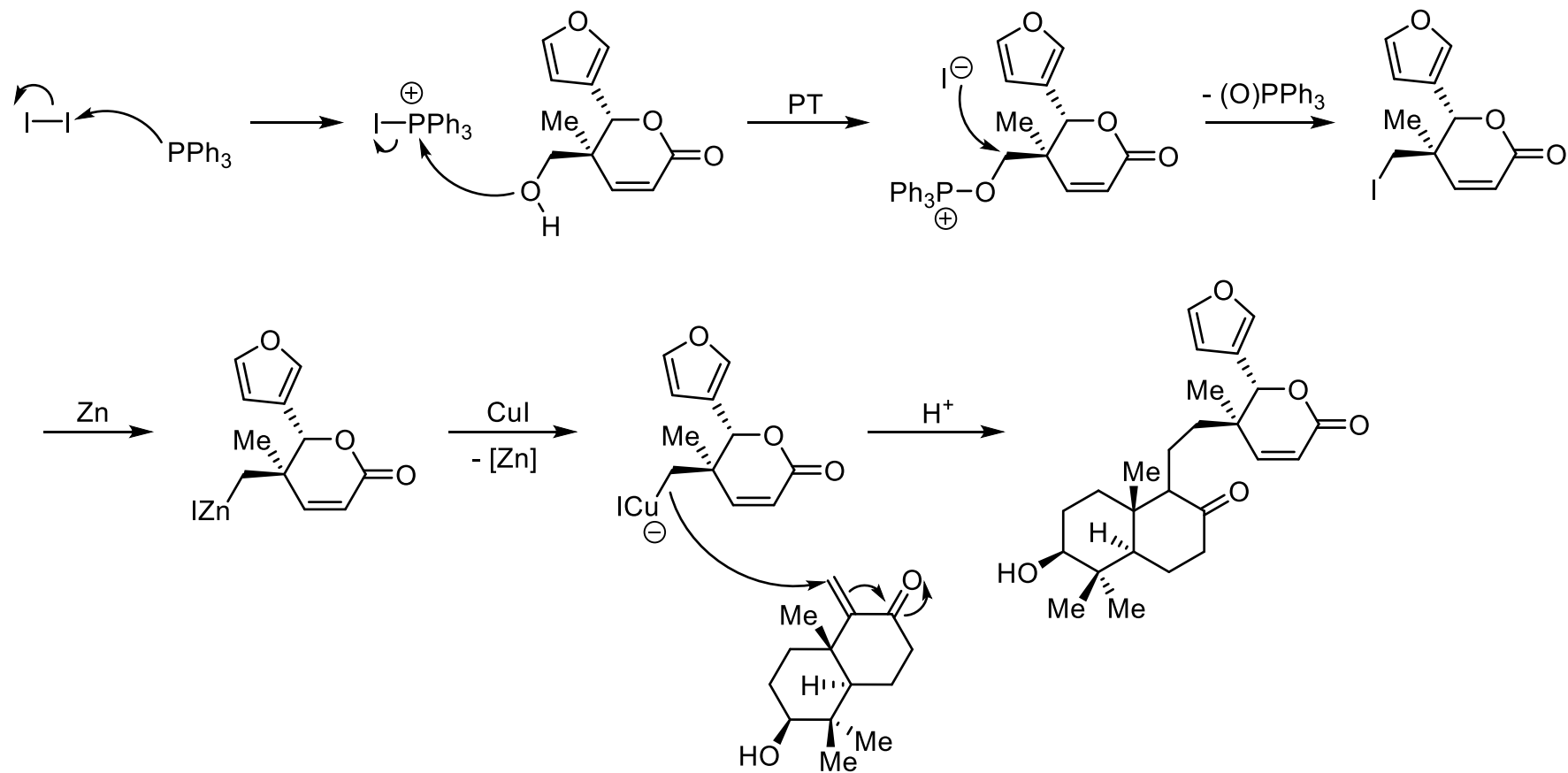


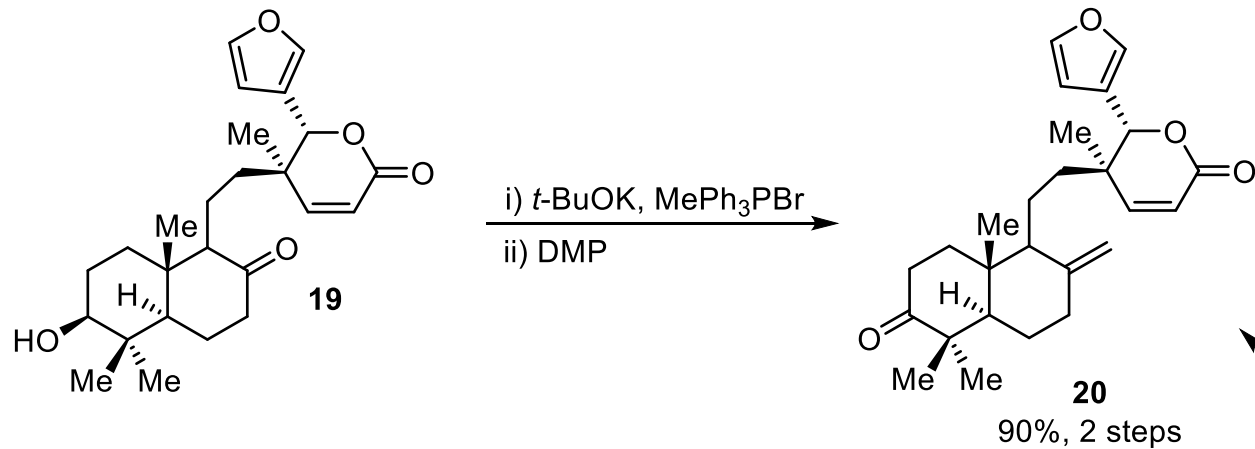




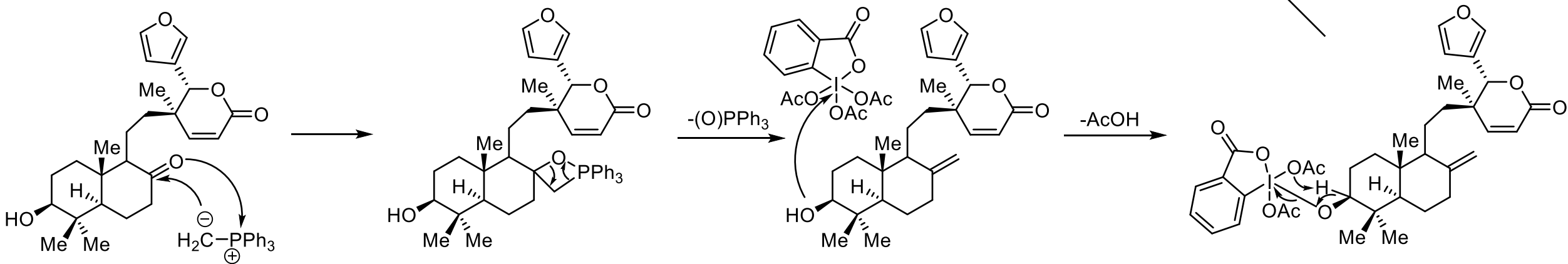


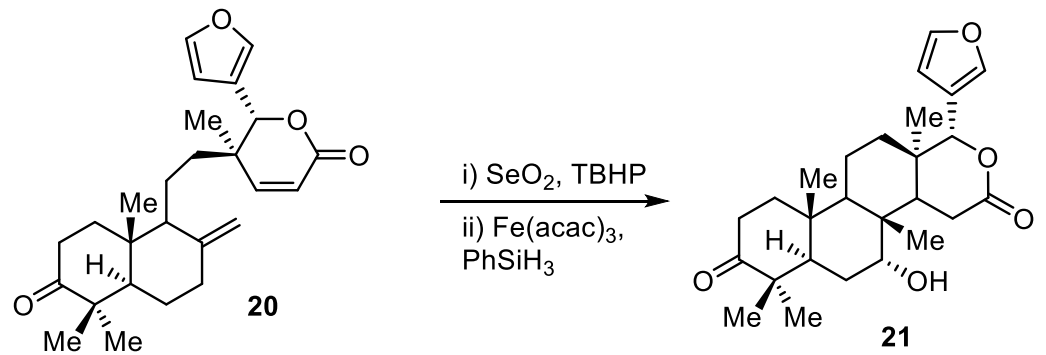
Appel reaction, metalation, 1,4-addition to enone 7



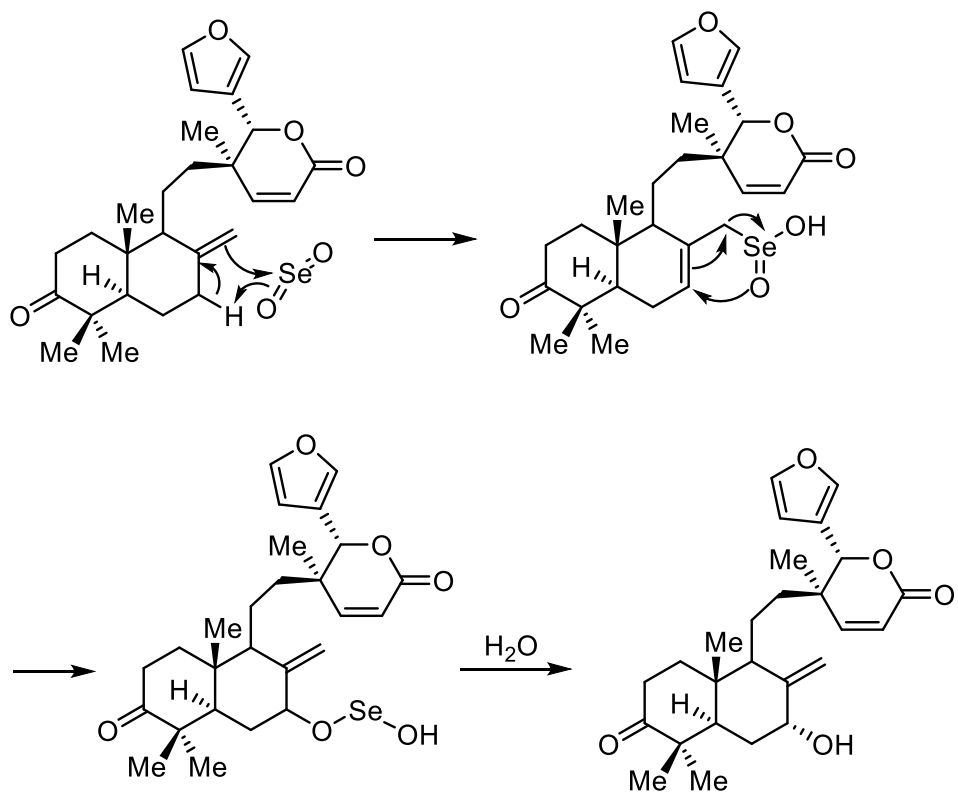


Wittig reaction, Dess-Martin periodinane oxidation





SeO₂-mediated allylic oxidation



HAT-based Giese addition

